



TITLE:

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(Commemoration Issue Dedicated to
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Retirement)

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CITATION:

Masuda, Tatsuo ...[et al]. Calorimetric Study of the Interaction of Montmorillonite with Amines (Commemoration Issue Dedicated to Professor Eiji Suito on the Occasion of his Retirement). Bulletin of the Institute for Chemical Research, Kyoto University 1975, 53(2): 147-152

ISSUE DATE:

1975-09-25

URL:

<http://hdl.handle.net/2433/76609>

RIGHT:

Calorimetric Study of the Interaction of Montmorillonite with Amines

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Received March 28, 1975

The interaction of montmorillonite with some amines was studied through the measurements of heat of immersion and adsorption.

The heats of immersion of montmorillonite into the solutions of *p*-phenylene diamine and benzidine at various concentrations in benzene were measured and the adsorption isotherms of these amines were obtained at the same time. From the results above and the heats of solution of amines in benzene, we derived differential and integral heat of adsorption for *p*-phenylene diamine and compared these values with the complex formation energy of benzidine.

The heat-of-immersion values showed the peculiarity of amines in comparison with other polar organic molecules. The amounts of adsorption and the heats of immersion are correlated with the basicity constants of amines. The amine-preadsorbed montmorillonite did not show the color reaction of benzidine blue, which suggests that aliphatic amine strongly interact with the acidic centers of montmorillonite, *i.e.*, aluminum ions at the crystal edges and transition metal ions with higher valencies and so on.

INTRODUCTION

Interest in the organo-clay chemistry has expanded in recent years. The interaction of organic molecules with montmorillonite clays has been studied by numerous investigators.¹⁾ To study clay-organic complexes, X-ray diffraction, electron diffraction, ESR, DTA and spectroscopic analysis have mainly been adopted. Regarding the interaction energy of polar molecules with clays, it has been more or less assumed that the adsorption mechanism proceeds through dipole-surface interaction such as O-H...O or N-H...O bonding to the surface.^{2,3)} On the other hand, K. K. Bissada *et al.*⁴⁾ have recently shown the effects of interlayer cations on adsorption process.

However, few attempts have been made to evaluate the complex formation energy. In this study, we measured the heat of immersion of montmorillonite into amines and discussed the formation of the stable complex on the surface.

EXPERIMENT

The montmorillonite used in this study was Wyoming Na-montmorillonite (API Clay Mineral Standard #25). Amines, alcohols, 1-nitropropane and benzene were all of high purity purchased at Wako Pure Chemical Co. They were all dehydrated using molecular sieve 4A.

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The heat of immersion and the heat of solution were measured at 25°C using a twin-type conduction microcalorimeter (Tokyo Riko Co. Ltd.).

The clay samples were prepared by the following way in order to measure the heat of immersion. The samples were dried in air about 3 hours at 200°C and about 0.6 g of air dried sample was weighed in a tarred glass ampoule and heat-treated at 200°C under 10^{-5} torr for 10 hours. The ampoule was sealed by fusing its neck in a flame and set in calorimeter. After they reached thermal equilibrium at 25°C, the ampoule was broken and clay sample was immersed into amines. The relative error in the calorimetric measurement was generally less than $\pm 3\%$ of the measured values.

The amounts of adsorption of *p*-phenylene diamine and benzidine were measured using a recording spectrometer (Shimadzu Model MPS-5000). As for other amines, the amounts of adsorption were measured by using a C.H.N. analyser. The samples for the latter measurements were previously washed 5 times with benzene.

The color reaction of montmorillonite with benzidine was observed by the following way. The montmorillonite sample dried in air was immersed in liquid amines, alcohols and 1-nitropropane and dried in air. The sample was then immersed in a benzidine-benzene solution and the change of color was observed.

In order to examine the possibility of displacement of Na^+ ions in montmorillonite by amines, the suspension of the amine-clay complex was centrifuged and the extracted Na^+ ions in the supernatant was measured by atomic absorption spectrophotometer (Perkin-Elmer 403).

RESULTS AND DISCUSSION

I. Heats of Immersion into Liquid Amines

Table I presents the observed values of heat of immersion of montmorillonite into various neutral amines, alcohols and the basal plane spacings from X-ray diffraction. In this table, basicity constants (K_b) and the amounts of adsorbed amines are also shown.

The heats of immersion into *n*-amines are about four times larger than those into *n*-propyl alcohol, *n*-butyl alcohol and 1-nitropropane. As to the series of *n*-amines, gradual increase of the heats of immersion are observed along with the molecular weight. This is probably due to the increasing contribution of van der Waals force with the chain length because their adsorbed amounts are almost the same each other.

In secondary and tertiary amines, the adsorbed amounts are less than those of primary amines, indicating that a smaller number of the molecules cover the clay surface because of the branched structures. This brings the lower heat-of-immersion values for the higher class amines in comparison with those of primary amines.

However, the converted values of their heat-of-immersion values into the unit of Kcal per mole of adsorbed amines (the last column of the table) are comparable or larger than those of primary amines. Among the aromatic amines, appreciable differences in the heat-of-immersion values are found in spite of their similarity in the steric hindrance.

The results of color reaction were as follows. The amine-preadsorbed montmorillonite did not show the color change of benzidine blue in benzene solution. On the other hand, the alcohol and nitro compounds-preadsorbed montmorillonite showed the clear color change of benzidine blue in the same solution. D. H. Solomon *et al.*⁵⁾ proposed

Calorimetric Study of the Interaction of Montmorillonite with Amines

Table I. The dipole moments and the basicities (K_b) of organic compounds used in this study and the observed values of basal plane spacings, $d(001)\text{\AA}$, heats of immersion, cal/g·clay and amounts of adsorption, meq/g·clay

| Sample | Dipole moment | K_b | $d(001)\text{\AA}$ | Cal/g·clay | ads. meq/g·clay | Kcal/Mol ^(a) |
|---------------------------------|---------------|-----------------------|--------------------|------------|-----------------|-------------------------|
| $n\text{-(CH}_2)_3\text{·NH}_2$ | 1.17 | 3.8×10^{-4} | 13.4 | 12.8 | 0.88 | 14.5 |
| $n\text{-(CH}_2)_4\text{·NH}_2$ | 0.92 | 4.4×10^{-4} | 13.4 | 14.5 | 0.90 | 16.1 |
| $n\text{-(CH}_2)_6\text{·NH}_2$ | 1.32 | 4.4×10^{-4} | 13.8 | 15.4 | 0.89 | 17.7 |
| $n\text{-(CH}_2)_8\text{·NH}_2$ | | 4.5×10^{-4} | | 15.2 | | |
| Diethylamine | 0.92 | 9.5×10^{-4} | 13.3 | 8.2 | 0.52 | 16.2 |
| Triethylamine | | 5.9×10^{-4} | 14.5 | 6.5 | 0.46 | 14.0 |
| E·D ^(b) | | 0.85×10^{-4} | 13.1 | 23.7 | | |
| Benzylamine | | 0.23×10^{-4} | 16.7 | 13.4 | 1.15 | 11.6 |
| Aniline | 1.48 | 4.4×10^{-10} | 15.1 | 2.7 | 0.42 | 6.4 |
| O-toluidine | | 2.5×10^{-10} | 16.7 | 2.6 | 0.48 | 5.4 |
| $n\text{-(CH}_2)_3\text{·OH}$ | | | 13.6 | 4.4 | | |
| $n\text{-(CH}_2)_4\text{·OH}$ | 1.69 | | 13.4 | 3.0 | | |
| $n\text{-(CH}_2)_3\text{·NO}_2$ | 3.59 | | 13.4 | 4.3 | | |

(a) These values are not exactly the same with the heat of adsorption but can be treated as an index of heat of adsorption.

(b) Ethelene diamine.

that the portions contributing to the color reaction of clay with aromatic diamine were aluminum ions in octahedral coordination exposed at the crystal edges and ferric ions located in the interior of the crystal lattices and exposed at the crystal edges. The results of color reaction suggest that neutral amines tend to so strongly coordinate with these acid centers on montmorillonite surface as to almost react chemically.

In the immersion processes, no displacement of Na^+ ions in montmorillonite by dehydrated amines could be observed. Only in amine-water solutions, the displacement of Na^+ ions by the amines was observed. However, we should notice that the amount of adsorption of primary amines approximately coincide with the cation exchange capacity of montmorillonite (C.E.C.=80–110 meq/100 g clay) as presented in Table I. Accordingly there might exists some possibility of formation of the coordination bond between amines with Na^+ ions at the clay surface due to the strong electron donating properties of amines as discussed by J. B. Van Assche *et al.*⁽⁶⁾

We could not recognize clear correlation between the dipole moments of amines and the heats of immersion. This suggests that the dipole-surface and the dipole-cation interactions are not the major mechanisms in the adsorption process of neutral amines on Na-montmorillonite.

In conclusion, neutral amines have a tendency of specific complex formation on Na-montmorillonite in comparison with alcohol and nitro-compounds. The larger the basicity, the greater is the electron donating tendency and it is a certainly important factor for intercalating ability and for the heat of adsorption of neutral amines.

II. The Estimation of Complex Formation Energy from Heat of Immersion

We measured the heats of immersion of montmorillonite into benzene solutions of

p-phenylene diamine and benzidine. These aromatic diamines are well known for their specific color reaction with montmorillonite.^{1a,5)}

The results of heats of immersion and adsorption isotherms are given in Fig. 1 and Fig. 2 as functions of added diamine. The amount of adsorption was spectroscopically measured by using the ultraviolet absorption band of diamine in benzene solution. The heat of immersion of montmorillonite into non-polar benzene was 1.53 cal/g·clay. The heats of solution of aromatic diamines in benzene are given in Fig. 3 as a function of the concentration. These heats of solution were all endothermal.

Generally, the heat of adsorption from solution is evaluated by the following equations.

$$\Delta H_{\text{ads}} = \Delta H_{\text{i}}(\text{sol.}) - \Delta H_{\text{i}}(\text{solv.}) + \Delta H_{\text{dil}}$$

$\Delta H_{\text{i}}(\text{sol.})$; Heat of immersion into solution.

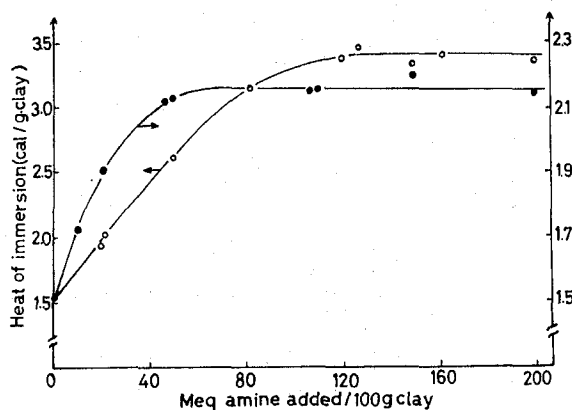


Fig. 1. Heats of immersion of montmorillonite into the solutions of *p*-phenylene diamine and benzidine.

right ordinate; benzidine

left ordinate; *p*-phenylene diamine

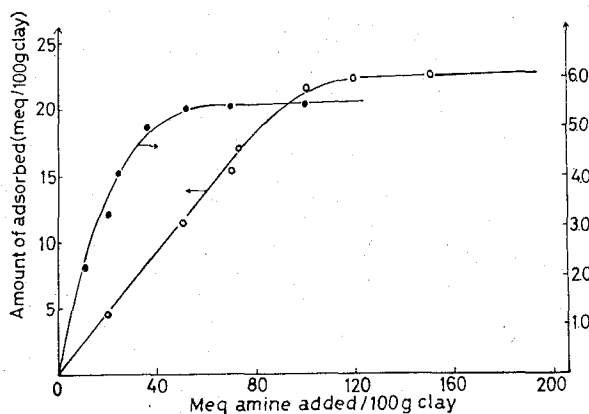


Fig. 2. Adsorption isotherms on montmorillonite at 25°C for *p*-phenylene diamine and benzidine.

right ordinate; benzidine

left ordinate; *p*-phenylene diamine

Calorimetric Study of the Interaction of Montmorillonite with Amines

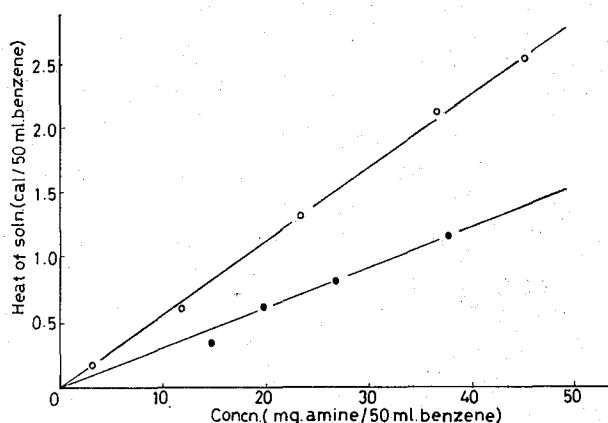


Fig. 3. Heats of solution of *p*-phenylene diamine (open circles) and benzidine (black circles) in benzene at 25°C.

$\Delta H_i(\text{solv.})$; Heat of immersion into solvent.

ΔH_{dil} ; Heat of dilution.

Here, we assume that the values of $\Delta H_i(\text{solv.})$ does not vary appreciably with the concentration. The calculated values of the complex formation energy by above equation are

$$H_{ads} = 21.9 (\text{Kcal/mol}) \text{ for } p\text{-phenylene diamine}^*$$

$$H_{ads} = 28.7 (\text{Kcal/mol}) \text{ for benzidine}$$

In Fig. 4 are also shown the differential and integral heat of adsorption of *p*-phenylene diamine that was estimated by combining with the heats of immersion, the

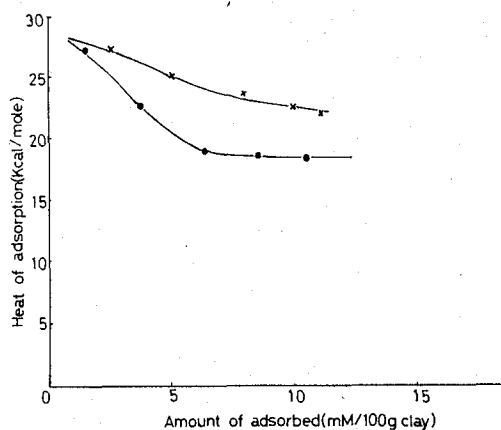


Fig. 4. Differential (lower curve) and integral (upper curve) heat of adsorption of *p*-phenylene diamine.

* These values were obtained by using the mean values of more than three values of the heat of immersion at the saturation of adsorption.

adsorption isotherms and the heats of solution of *p*-phenylene diamine *etc.* For benzidine, we could not obtain the reliable values of differential heat of adsorption because of their less amount of adsorption.

The results of X-ray diffraction measurements on (001) spacing provided no evidence for intercalation of both aromatic diamines. So, the complexes seem to be formed only at the external surface of Na-montmorillonite in benzene solution. The effectiveness of acid centers of montmorillonite to color reaction has been proposed by several workers as previously mentioned. The specific surface area of Na-montmorillonite measured by nitrogen adsorption at 77°K is 22.2 m²/g. If the adsorption of diamine occurred uniformly at the external surface, the cross sectional area is derived to be about 35 Å² for *p*-phenylene diamine and larger than 100 Å² for benzidine. This unreasonably large value for benzidine suggests that montmorillonite-benzidine complex only occurred in a portion of the montmorillonite surface. The integral heat of adsorption of *p*-phenylene diamine in Fig. 4 at the same amounts of adsorption as the saturated amounts of adsorption of benzidine is almost the same to the complex formation energy of benzidine. Therefore, the complex formation mechanism of *p*-phenylene diamine may possess more complicated steps in addition to the mechanism of benzidine-complex formation. But it is not still clear whether this difference depends on the higher basicity of *p*-phenylene diamine than benzidine or on the other factors.

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